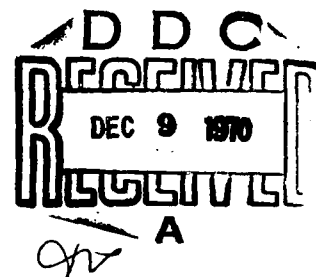


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## Determination of Trace Contaminants in Air by Concentrating on Porous Polymer Beads

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With the ever increasing need for the determination of trace contaminants in complex mixtures, the development and use of selective detectors (1) has become very important in gas chromatography. The selective detector eliminates superfluous peaks from the chromatograms and thus makes the qualitative and quantitative analysis of complex mixtures much easier. However, the best detector for a particular analysis often cannot be used because of its lack of sensitivity. Various concentrating techniques, most of which employ cryogenic trapping, have been reported in the literature, and have been reviewed by Altshuller (2). A method has been developed for concentrating gas samples at room temperature on porous polymer beads which eliminates the use of cold traps or cold columns, and gives on-column injection. The gas sample is concentrated on the same column that is subsequently used for the gas chromatographic analysis.

For the determination of chlorinated and brominated hydrocarbons, three selective detectors are available, electron capture, stacked thermionic flame, and microcoulometer.

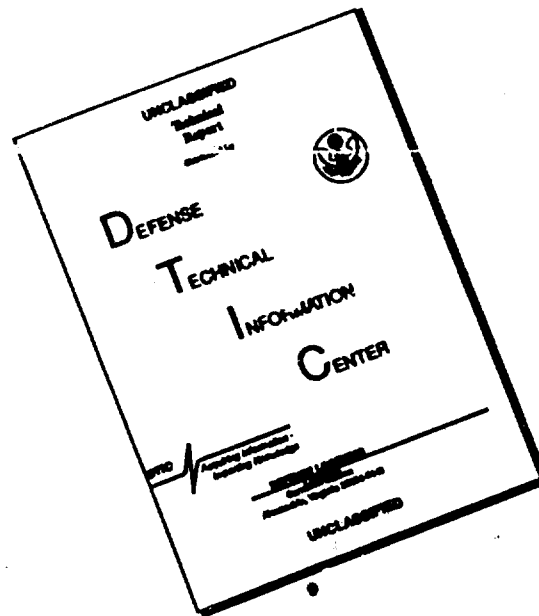
The electron capture detector has the disadvantages of having only a very narrow linear range, requiring a separate calibration factor for each halogenated compound, and being relatively insensitive to many chlorinated compounds. A compound which captures electrons weakly and whose chromatographic peak falls adjacent to a strongly capturing compound is completely obscured by a much smaller quantity of the strong electron capturer. There are very few papers in the literature where the stacked thermionic flame detector has been used for routine determinations.

It was felt that the microcoulometer was potentially the best detector for chlorinated hydrocarbons, because its response (3) should be directly related through Coulomb's law to the number of chlorine atoms in the molecule. There are two drawbacks to the microcoulometer, slow response and lack of sensitivity. The range of detection of the microcoulometer has been reported (3) to be from 0.1 to 1000  $\mu\text{g}$  of chloride ion. Because trace analysis in gas chromatography is usually considered to be in the range of 1 ppb to 10 ppm by volume, the sensitivity of this detector is not sufficient with

- (1) E. Cremer, "Advances in Gas Chromatography," Preston Technical Abstracts Co., Evanston, Ill., 1967, p 52.  
(2) H. P. Altshuller, *J. Gas Chromatogr.*, 1, (7) 6 (1963).

- (3) D. M. Coulson and L. A. Cavanagh, *ANAL. CHEM.*, 32, 1245 (1960).

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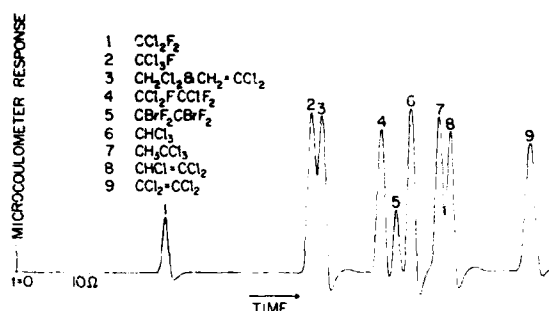


Figure 1. Coulometric response for halogenated hydrocarbons in  $2 \pm 1$ -ppm range using 100-ml sample loop

the normal chromatographic air sample of 5 to 10 ml. In order to obtain the required sensitivity, a concentrating technique is needed.

It had been reported previously by Hollis (4) that the retention times of low molecular weight hydrocarbons and halogenated hydrocarbons were quite long on porous polyaromatic polymer bead columns as compared to gas-liquid chromatographic columns. These long retention times make it possible to concentrate air samples on the chromatographic column at room temperature, and subsequently elute the components as symmetrical peaks by temperature programming. The sample components apparently remain as a narrow band on the column until its temperature is raised above ambient. The slow response of the microcoulometer is not of consequence, as it is compensated for by the long and varied retention times of the low molecular weight halogenated hydrocarbons on the porous polymer beads. Also the fact that water does not interfere and is eluted as an early peak without tailing, eliminates the necessity of drying the sample before injection.

#### EXPERIMENTAL

**Equipment and Chemicals.** The on-column concentrating technique was developed using Porapak Q and S obtained from Waters Associates, Inc. The 80-100 mesh Porapaks were packed in 6-foot  $\times$   $\frac{1}{4}$ -inch stainless steel columns. The chromatograph used was a Microtek MT-220 equipped with a Dohrmann Microcoulometer operating in an oxidative mode with a silver cell. The chromatograph was also equipped with a multifunctional programmer and Carle 8-port sampling valves. The standard gas mixtures were prepared in Alloy Products Corp. gas bottles made of stainless steel having a volume of 1.7 liters. The chlorinated hydrocarbons were purchased from Chem Service Inc. The chlorofluorocarbons were obtained from DuPont.

The gas mixtures were prepared by dilution techniques. In the case of liquid halogenated compounds, the calculated volume of the liquid was injected with a microsyringe, through a septum, into an evacuated gas bottle. The bottle was then pressurized to 300 psia with air or helium. For lower dilutions, aliquots of the original mixtures were further diluted.

**Procedure.** The halogenated compounds that have been determined by this technique in the 10-ppb-by-volume range are given in Table I. Care must be taken to prevent adsorption in the sample loop and sample valve. There was no apparent sample loop adsorption because of the high volatility of the compounds analyzed and the length of time for the injection.

Table I. Halogenated Hydrocarbons Determined by On-Column Concentrating

Compounds	Boiling point, °C
CH <sub>2</sub> Cl	-24
CCl <sub>2</sub> F <sub>2</sub> , (Freon-12)	-29.79
CH <sub>2</sub> =CHCl	-13.9
CH <sub>2</sub> Cl <sub>2</sub>	40.2
CClF <sub>2</sub> -CClF <sub>2</sub> , (Freon-114)	3.77
CCl <sub>3</sub> F, (Freon-11)	23.77
CH <sub>2</sub> =CCl <sub>2</sub>	37
cis-CHCl=CHCl	60
trans-CHCl=CHCl	48.3
CCl <sub>3</sub> F-CClF <sub>2</sub> , (Freon-113)	47.57
CBrF <sub>2</sub> -CBrF <sub>3</sub> , (Freon-114B-2)	47.26
CHCl <sub>3</sub>	61.2
CH <sub>2</sub> CCl <sub>3</sub>	74.0
CHCl=CCl <sub>2</sub>	87.2
CCl <sub>2</sub> =CCl <sub>2</sub>	121.2

The type of porous polymer beads selected and the particular temperature program used depends on the mixture to be analyzed. A portion of the air sample to be analyzed is put in a 100- or 500-ml sample loop. Care must be taken that the column oven is equilibrated at some temperature between 30 to 50 °C. This equilibration temperature must be the same for each analysis or the retention times of the components of the standard and the sample will vary slightly. The sample is injected into the column over a 5-minute period, with helium used as a carrier. The sample valve is left in the inject position throughout the entire analysis. The flow rate of the carrier gas must be great enough to transfer the sample from the sample loop to the column in the allotted time. The temperature of the column is then raised at the maximum heating rate to 100 °C and held at this temperature for 5 minutes. The appropriate temperature program for the mixture is then followed to elute the sample. The program used for the mixtures in this paper was 10 °C/minute from 100 to 120 °C, 2 °C/minute from 120 to 136 °C, and 10 °C/minute from 136 to 166 °C. The column then was heated at the maximum rate to 210 °C and held there until the tetrachloroethene was eluted.

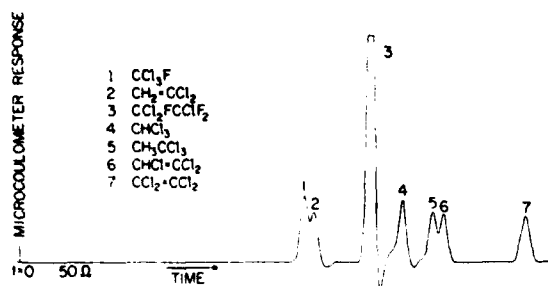
After analyzing numerous air mixtures, it becomes necessary to "clean" the porous-polymer-bead column of higher molecular weight compounds present in the mixtures. This is accomplished by raising the column temperature to 210 °C at night so that the helium carrier purges the column. It is necessary to do this in order for the retention times of the standards to remain constant. The purging of the column could also be accomplished by backflushing the column.

#### RESULTS AND DISCUSSION

A mixture of some of the compounds in Table I in the  $2.0 \pm 1$ -ppm range (except for the CCl<sub>2</sub>F<sub>2</sub>) is shown in Figure 1. The elution time for the tetrachloroethene is 38 minutes on Porapak S. A 100-ml sample loop was employed for this analysis. Figure 2 shows a chromatogram of a sample in the  $20 \pm 10$ -ppb range using a 500-ml sample loop. The CCl<sub>2</sub>FCClF<sub>2</sub> peak is too large because of the contamination of the sample bottle valve with this compound in its manufacture. The brominated compound is not quantitative in the silver cell because of the formation of the hypobromite. In making standard samples in the ppb range, difficulties are often encountered, particularly with CCl<sub>2</sub>FCClF<sub>2</sub> because of contamination from the dilution gas and equipment.

The technique of on-column concentration of large air samples has also been used with a hydrogen flame detector.

(4) O. L. Hollis, ANAL. CHEM., 38, 309 (1966).



**Figure 2. Coulometric response for halogenated hydrocarbons in 20-  $\pm$  10-ppb range using 500-ml sample loop**

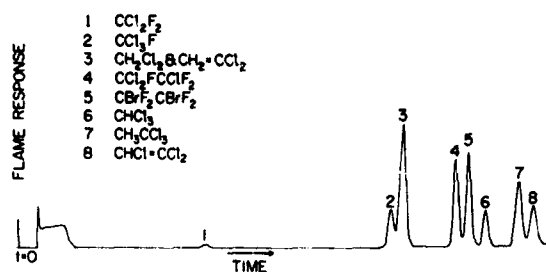
**Table II. Accuracy and Precision of On-Column Concentrating Technique with Porapak Q Column**

Compound	Prepared standard, ppm	Determined by coulometric detector, ppm
$\text{CH}_2=\text{CCl}_2$	1.0	0.96, 1.04, 1.02
$\text{CCl}_2\text{F}-\text{CClF}_2$	1.0	0.99, 1.01, 0.99
$\text{CHCl}_3$	1.0	0.98, 0.92, 1.01
$\text{CH}_2\text{CCl}_3$	1.0	0.95
$\text{CH}_2=\text{CHCl}$	2.5	2.5

Figure 3 shows the flame response to a mixture in the 1-ppm range using a 100-ml sample loop. There is an initial upset in the flame base line when the large volume samples are injected, but this settles down before the first peak is eluted.

The on-column concentrating technique for gas samples eliminates the need for cold traps and cold columns. It is conceivable that much larger samples could be used, limited only by the physical length of time required to put the sample on the column.

The base line of the microcoulometer is not affected by the temperature programming of porous polymer beads, although there is a slight degradation of the polymer at the high tem-



**Figure 3. Flame ionization response for halogenated hydrocarbons in 1-ppm range using 100-ml sample loop**

peratures. Because no chlorinated product is evolved in this degradation, the detector does not respond.

The quantitative accuracy and precision of the on-column concentrating technique were determined by standards containing only one halogenated compound in air. The standards were prepared to have a concentration of 1.0 and 2.5 ppm by volume. The response of the standards when chromatographed using the on-column concentrating technique was related through Coulomb's law and the concentration was determined. This value was then compared to the prepared concentration. These data are presented in Table II. The data show that the method is quantitative and thus there is no loss of sample on the column or elsewhere. The greatest problems in determining the quantitative accuracy of the method are encountered in preparing the standards in the ppb range and not in the determinations.

The on-column concentrating technique has been used routinely in studying trace contaminants in closed environmental systems and in air pollution studies at this Laboratory.

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